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Electrosynthesis of a $Sc_3N@I_h$-C_{80} Methano Derivative from Trianionic $Sc_3N@I_h$-C_{80}

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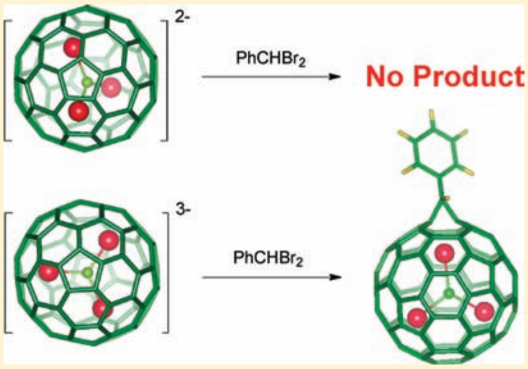
Supporting Information



ABSTRACT: The electrosynthetic method has been used for the selective synthesis of fullerene derivatives that are otherwise not accessible by other procedures. Recent attempts to electrosynthesize $Sc_3N@I_h$-C_{80} derivatives using the $Sc_3N@I_h$-C_{80} dianion were unsuccessful because of its low nucleophilicity. Those results prompted us to prepare the $Sc_3N@C_{80}$ trianion, which should be more nucleophilic and reactive with electrophilic reagents. The reaction between $Sc_3N@C_{80}$ trianions and benzal bromide ($PhCHBr_2$) was successful and yielded a methano derivative, $Sc_3N@I_h$-$C_{80}(CHPh)$ (**1**), in which the >CHPh addend is selectively attached to a [6,6] ring junction, as characterized by MALDI−TOF mass spectrometry and NMR and UV−vis−NIR spectroscopy. The electrochemistry of **1** was studied using cyclic voltammetry, which showed that **1** exhibits the typical irreversible cathodic behavior of pristine $Sc_3N@I_h$-C_{80}, resembling the behavior of other methano adducts of $Sc_3N@I_h$-C_{80}. The successful synthesis of endohedral metallofullerene derivatives using trianionic $Sc_3N@I_h$-C_{80} and dianionic $Lu_3N@I_h$-C_{80}, but not dianionic $Sc_3N@I_h$-C_{80}, prompted us to probe the causes using theoretical calculations. The $Sc_3N@I_h$-C_{80} trianion has a singly occupied molecular orbital with high spin density localized on the fullerene cage, in contrast to the highest occupied molecular orbital of the $Sc_3N@I_h$-C_{80} dianion, which is mainly localized on the inside cluster. The calculations provide a clear explanation for the different reactivities observed for the dianions and trianions of these endohedral fullerenes.

INTRODUCTION

The discovery in 1999 by Stevenson et al.[1] of a family of endohedral fullerenes encapsulating trimetallic nitride clusters, $Er_xSc_{3-x}N@C_{80}$ (x = 0−3), opened a new era in the field of endohedral fullerenes. Since then, trimetallic nitride template endohedral metallofullerenes (TNT-EMFs)[2−7] have been extensively studied, mainly because of their unique electronic properties resulting from significant charge transfer from the internal cluster to the carbon shell. These interesting properties have potential applications in many fields, such as in photovoltaics[8−12] and as biological diagnostic and therapeutic agents.[13−16] To pursue applications, it is necessary to develop synthetic strategies for the preparation of soluble derivatives. Some established reactions such as Diels−Alder,[17,18] Bingel−Hirsh,[19−21] 1,3-dipolar cycloaddition,[22−27] free radical addition,[28−32] and [2 + 2] addition reactions[33] have been used to functionalize EMFs. It is important to explore new strategies for synthesizing difficult-to-prepare TNT-EMF derivatives.

Electrosynthetic methods to synthesize fullerene derivatives were developed in 1993,[34] when a reaction involving a dianionic fullerene species generated using electrochemical reduction was reported for the first time.[34] Since then, electrosynthetic methods have been used as an alternative for functionalization of fullerenes. New fullerene derivatives with high regioselectivity that are not accessible using more conventional methods have been synthesized via the electrosynthetic route.[35−42] Electrochemical reduction methods were also discovered to be very useful for selective and efficient removal of cyclopropano addends from fullerenes (a process called the retro-cyclopropanation reaction),[43−51] making them synthetically useful in the preparation of the desired fullerene derivatives through a protection−deprotection strategy.[48] Such cyclopropane rings are highly stable and cannot be removed thermally or by wet-chemical methods. This electrochemically induced retro-cyclopropanation reaction was also employed as a synthetic tool in the preparation of fullerene isomers[45] and enantiomerically pure fullerenes[44] that in some cases were otherwise not accessible.

Anionic fullerenes are nucleophilic reagents prepared via electrochemical reduction. It is worth noting that different fullerene anionic states can lead to different products even under the same reaction conditions as a result of their different nucleophilicities. For example, the reaction between C_{60}^{2-} and benzyl bromide in benzonitrile affords 1,4-$(PhCH)_2C_{60}$ as the major product, while the reaction of C_{60}^{3-} gives a novel

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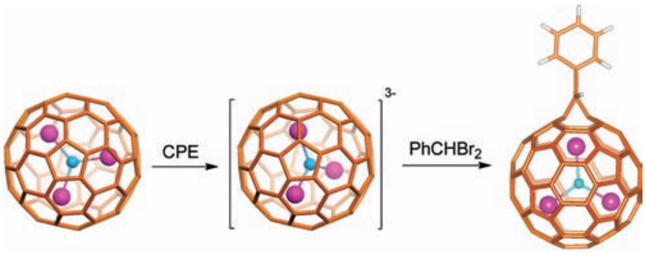
heterocyclic derivative of C_{60} (1,4-dibenzyl-2,3-cyclic phenylimidate C_{60}) as the major product and 1,4-$(PhCH)_2C_{60}$ as the minor one.[52] Two new reactions initiated by fullerene trianions resulted in two new compounds that cannot be prepared from C_{60}^{2-},[52−54] showing that different fullerene anion species exhibit different reactivities, with the trianions being more nucleophilic and consequently more reactive than the corresponding dianions. Early studies using spectroscopy and voltammetry showed that fullerene trianions are unstable and, as expected, more reactive than the dianions.[55−57]

The electrosynthetic method, however, has not been widely applied to EMFs, and the reactivities of anionic EMF species have not been extensively studied. Very recently, the electroreductive synthetic method was applied to $M_3N@I_h$-C_{80} (M = Sc, Lu), and very different reactivities were observed for $[Sc_3N@I_h\text{-}C_{80}]^{2-}$ and $[Lu_3N@I_h\text{-}C_{80}]^{2-}$ with electrophiles.[58] Under identical conditions, $[Lu_3N@I_h\text{-}C_{80}]^{2-}$ was observed to react readily while $[Sc_3N@I_h\text{-}C_{80}]^{2-}$ was completely unreactive. Computational studies showed that the charge density of the highest occupied molecular orbital (HOMO) of $[Sc_3N@I_h\text{-}C_{80}]^{2-}$ is mainly localized on the encapsulated cluster and not on the cage, whereas the opposite is true for $[Lu_3N@I_h\text{-}C_{80}]^{2-}$. These observations prompted us to probe the reactivity of $[Sc_3N@I_h\text{-}C_{80}]^{3-}$, which has a higher charge density and thus would be expected to be more reactive with electrophiles. Here we report the first successful synthesis of a derivative of $Sc_3N@I_h$-C_{80} in reasonable yields obtained from the nucleophilic reaction of $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ and benzal bromide ($PhCHBr_2$).

■ RESULTS AND DISCUSSION

Preparation and Isolation of Products 1 and 2. The $Sc_3N@C_{80}$ sample was reduced to its trianion in *o*-dichlorobenzene (*o*-DCB) containing 0.1 M tetra-*n*-butylammonium perchlorate (*n*-Bu_4NClO_4) as the supporting electrolyte under controlled-potential electrolysis (CPE) at −2.10 V versus a silver wire reference electrode under an argon atmosphere (Scheme 1). An excess of $PhCHBr_2$ was then added to the resulting solution in one portion. The reaction was allowed to proceed for 2 h with stirring, and then the solution was electrochemically oxidized by setting the potential to 0 V. Thus, the starting material was recovered by oxidizing the remaining unreacted $[Sc_3N@C_{80}]^{3-}$ to $Sc_3N@C_{80}$. The solvent was evaporated, and 100 mL of methanol was added to dissolve the supporting electrolyte for removal by filtration. The residue was dried in a vacuum oven. The reaction mixture was dissolved in toluene and initially separated using a Buckyprep column to isolate fraction A and recover the unreacted $Sc_3N@I_h$-C_{80}, as shown in Figure 1a. A second chromatographic separation using a 5PBB column revealed that fraction A contained two compounds, **1** and **2** (Figure 1b) that could not be separated on a Buckyprep, Buckyprep-M, or 5PYE column. **1** and **2** were assigned to benzal (>CHPh) monoadducts of $Sc_3N@C_{80}$ on the basis of MALDI−TOF mass spectrometry (MS) (see Figure 2a,b), and further characterizations and analyses confirmed that **1** is a product resulting from the I_h isomer of $Sc_3N@C_{80}$, with a yield of ca. 27% based on the amount of $Sc_3N@C_{80}$ consumed, while **2** is most likely the corresponding product of the D_{5h} isomer, which was present in small amounts in the starting material. The yield of **2** was not determined, as the initial amount of $Sc_3N@D_{5h}$-C_{80} in the original sample was unknown. Careful analysis of the starting endohedral fullerene sample using a 5PYE column and a Buckyprep column showed that it was a mixture of the I_h and D_{5h} isomers of $Sc_3N@C_{80}$.[1,59]

Scheme 1. Nucleophilic Reaction of $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ with Benzal Bromide ($PhCHBr_2$)



MS, Spectroscopic, and CV Studies of the Adducts. The MALDI−TOF mass spectrum of **1** (Figure 2a) showed the formation of the target monoadduct $Sc_3N@I_h$-C_{80}(CHPh) at *m*/*z* 1198.983. The peak at *m*/*z* 1108.878 corresponds to the loss of the addend (>CHPh) to yield $Sc_3N@I_h$-C_{80}. Compound **2** was also characterized by MALDI−TOF MS (Figure 2b). The molecular ion peak appeared at *m*/*z* 1198.969, corresponding to another >CHPh functionalized monoadduct of $Sc_3N@C_{80}$. **2** had to be a regioisomer of **1** or the corresponding adduct of the D_{5h} isomer of $Sc_3N@C_{80}$. Although it could not be unambiguously established by ^{13}C NMR spectroscopy because of the small amount of sample, we assigned compound **2** as the [6,6] adduct of the D_{5h} isomer since we established the presence of this isomer in the starting material and it is known to be more reactive than the I_h isomer. In addition, previous reactions of dianionic fullerenes (C_{60}^{2-} and $[Lu_3N@I_h\text{-}C_{80}]^{2-}$)[41,58] with Br_2CHPh also led to the formation of [6,6] adducts. Although the mass spectrum showed that compound **1** is a monoadduct of $Sc_3N@I_h$-C_{80}, since there are two types of double bonds ([5,6] and [6,6] bonds) on the I_h-C_{80} cage where addition could take place, the position of the addend was not known. Therefore, the structure of **1** was further analyzed by proton NMR spectroscopy. Attempts to run the NMR experiment for **2** failed because of the limited amount of sample.

A [6,6] addition on an I_h-C_{80} cage produces a pair of enantiomers that are indistinguishable by NMR spectroscopy, whereas addition at a [5,6] ring junction leads to two sets of nonequivalent proton signals from the functional group due to the lack of symmetry for this addition pattern.[12,24,58] The ^1H NMR spectrum of **1** recorded in CS_2/DMSO-d_6 showed only one set of signals (Figure 2c), indicating that the addition pattern of **1** must be symmetric. The methine proton is characterized by a single resonance at 5.44 ppm, in agreement with the reported resonance at 5.37 ppm for the methine proton of $Lu_3N@I_h$-C_{80}(CHPh). Resonances corresponding to the phenyl protons were observed at 7.74 ppm (d, *J* = 7.5 Hz, 2H) and 7.27 ppm (m, 3H) with an integration ratio of 2:3. The ratio of the peak area of the methine proton to that of the phenyl protons was 1:5, consistent with the presence of the benzal group. The NMR data for **1** agree with the reported assignment for the monobenzal adduct of $Lu_3N@I_h$-C_{80},[58] suggesting a [6,6] open-cage structure like that of $Lu_3N@I_h$-C_{80}(CHPh). However, since [6,6] closed-cage structures have also been reported for some derivatives of $Sc_3N@I_h$-C_{80},[27,33] ^1H NMR spectroscopy could not establish whether the product was a closed-cage cyclopropane derivative or an open-cage fulleroid on a [6,6] bond. UV−vis−NIR spectroscopy can be

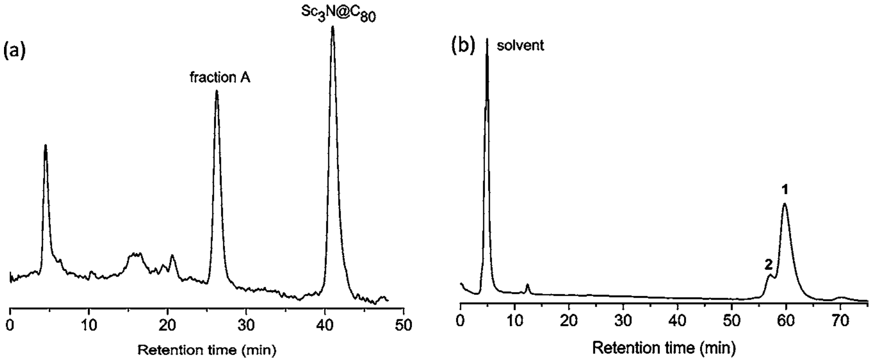


Figure 1. (a) HPLC trace of the crude product obtained from the reaction between $[Sc_3N@C_{80}]^{3-}$ and $PhCHBr_2$. Conditions: Buckyprep column (φ 10 × 250 mm) eluted with toluene at a flow rate of 4 mL/min; wavelength, 320 nm. (b) HPLC profile of fraction A isolated using the Buckyprep column. Conditions: 5PBB column (φ 10 × 250 mm) eluted with toluene at a flow rate of 4 mL/min; wavelength, 320 nm.

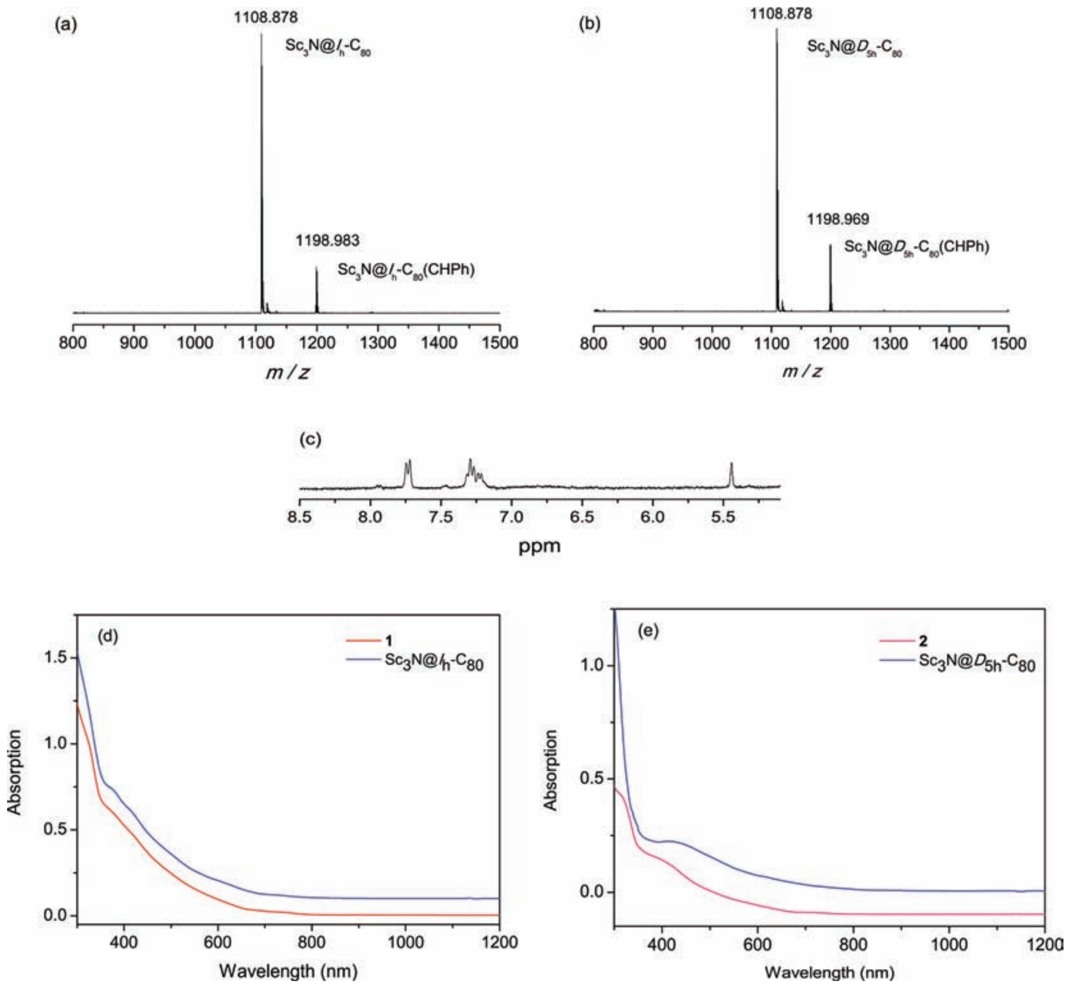


Figure 2. (a, b) MALDI−TOF mass spectra of (a) **1** and (b) **2** in positive-reflection mode. (c) Proton NMR spectrum of **1** in CS_2; DMSO-d_6 was used as an external reference. (d, e) UV−vis−NIR absorption spectra of (d) **1** and pristine $Sc_3N@I_h$-C_{80} and (e) **2** and pristine $Sc_3N@D_{5h}$-C_{80}.

used as a complementary tool to determine whether the fullerene monoadducts are open-cage fulleroids or closed-cage cyclopropane derivatives.[10,12,20,28,58] As shown in Figure 2d, pristine $Sc_3N@I_h$-C_{80} and derivative **1** exhibit almost identical absorption spectra. Thus, the electronic structure of the C_{80} chromophore is minimally disturbed by the presence of the functional groups, suggesting a [6,6] open-cage fulleroid structure for **1**.[12,28] The available amount of **2** was sufficient to record a UV−vis−NIR spectrum (Figure 2e), which was very similar to that of $Sc_3N@D_{5h}$-C_{80}, indicating that **2** likely corresponds to an open-cage structure. In addition, the UV−vis−NIR spectra of various $Sc_3N@I_h$-C_{80} anions along with that of $Sc_3N@I_h$-C_{80} were analyzed; the results are shown in the Supporting Information, and no significant differences were observed for the different anionic states.

Another valuable technique that has been extensively applied to analyze the monoadducts of TNT-EMFs is cyclic voltammetry (CV). Analysis of the electrochemical properties of TNT-EMF adducts from previous reports shows that [5,6] adducts typically display reversible cathodic electrochemical behavior[25] while [6,6] adducts in general exhibit irreversible behavior.[19,20,25] The cyclic voltammogram of compound **1** (Figure 3) showed electrochemically irreversible cathodic behavior analogous to that observed for the pristine fullerene[25] and the corresponding $Lu_3N@I_h$-C_{80} adduct[58] and similar to that of Bingel−Hirsch cyclopropanation[60−62] derivatives of TNT-EMFs[19,25] and of some [6,6] open-age TNT-EMF fulleroids.[10] Consequently, the adduct is most likely a [6,6] open-cage fulleroid, consistent with the results deduced from the NMR and UV−vis−NIR experiments. It is worth mentioning that there are some recently reported examples of $Sc_3N@I_h$-C_{80} [6,6] adducts displaying reversible reductive electrochemical behavior.[33,63] Those adducts contained closed surfaces on which the fullerene C−C bond with the addend attached was elongated but not fully broken. For **1** and other TNT-EMF Bingel−Hirsch products possessing open fullerene C−C bonds where the addends are located, the delocalized electronic structure of the cage is retained, and the electrochemical behavior is similar to that of the parent TNT EMFs. The combined NMR, UV−vis−NIR, and electrochemistry data indicate that compound **1** is a [6,6] open-cage fulleroid of $Sc_3N@I_h$-C_{80}.

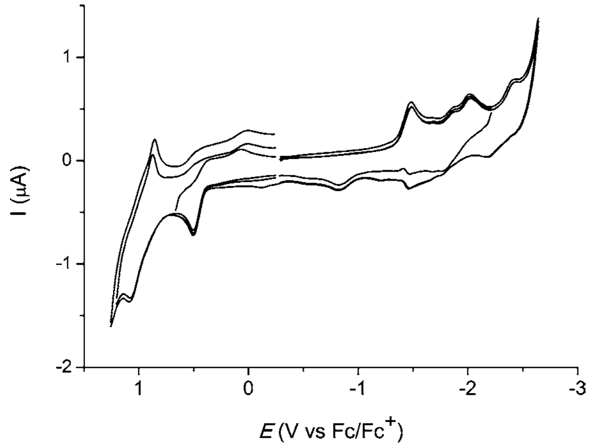


Figure 3. Cyclic voltammogram of **1** recorded in a 0.05 M solution of *n*-Bu_4NPF_6 in *o*-DCB at a scan rate of 100 mV/s.

Table 1 shows the electrochemical potentials of **1** along with those of pristine $Sc_3N@I_h$-C_{80} and the corresponding $Lu_3N@I_h$-C_{80} adduct. The processes for **1** resemble those for the $Sc_3N@I_h$-C_{80} Bingel−Hirsch cyclopropanation adducts reported by Echegoyen and co-workers.[19] The first reduction potential of **1** is negatively shifted by 220 mV compared with that of pristine $Sc_3N@I_h$-C_{80}, and this is similar to the behavior of the corresponding $Lu_3N@I_h$-C_{80} adduct. The first reduction potential is 100−240 mV more negative than those of the $Sc_3N@I_h$-C_{80} Bingel−Hirsch cyclopropanation adducts.[19] The second and third reductions are cathodically shifted by 390 and 30 mV, respectively, relative to the corresponding reductions for $Sc_3N@I_h$-C_{80}. Quasi-reversible and irreversible anodic electrochemical behavior with E_{pa} values of +1.08 and +0.50 V vs Fc/Fc$^+$, respectively, was observed for **1**, similar to that for pristine $Sc_3N@I_h$-C_{80}. $Sc_3N@I_h$-C_{80}(CHPh) has the most negative first reduction potential of any reported $Sc_3N@I_h$-C_{80} derivative,[8,9,19,64] and the value is comparable to those of $Lu_3N@C_{80}$−PCBM and $Lu_3N@C_{80}$−PCBH, which were reported to be outstanding acceptor materials in organic photovoltaic devices because of their high lowest unoccupied molecular orbital (LUMO) levels.[10]

Table 1. Redox Potentials of $Sc_3N@I_h$-C_{80}, Product 1, and the Corresponding $Lu_3N@I_h$-C_{80} Product[a]

	$E^{+/2+}$ (V)	$E^{0/+}$ (V)	$E^{0/-}$ (V)	$E^{-/2-}$ (V)	$E^{2-/3-}$ (V)
$Sc_3N@I_h$-C_{80}[b]	+1.09	+0.59	−1.26	−1.62	−2.37
$Sc_3N@I_h$-C_{80}(CHPh)	+1.08	+0.50	−1.48	−2.01	−2.40
$Lu_3N@I_h$-C_{80}(CHPh)[c]	+1.10	+0.59	−1.49	−1.95	−2.32

[a] Potentials are in V vs Fc/Fc$^+$. [b] From ref 25. [c] From ref 58.

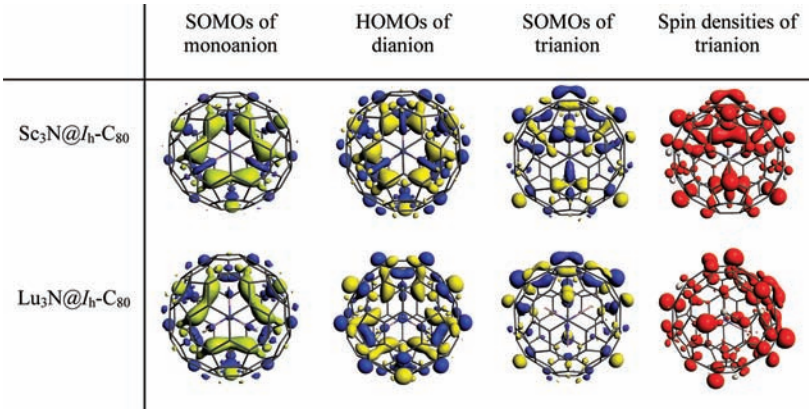
Theoretical Calculations on the Anionic Forms of $Sc_3N@I_h$-C_{80} and $Lu_3N@I_h$-C_{80}. To rationalize the causes for the different reactivities of $[Sc_3N@I_h\text{-}C_{80}]^{2-}$ and $[Sc_3N@I_h\text{-}C_{80}]^{3-}$, density functional theory (DFT) analyses of the different anionic forms were performed. DFT calculations have been extensively used to analyze the reactivity and selectivity of various fullerenes.[53,65−70] In our previous report, we found that $[Sc_3N@I_h\text{-}C_{80}]^{2-}$ exhibited lower nucleophilicity than $[Lu_3N@I_h\text{-}C_{80}]^{2-}$, and the results were explained by the shape and localization of the frontier molecular orbitals (MOs).[71] In the present report, the reaction between $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ and benzal bromide under the same conditions used to study that of $[Lu_3N@I_h\text{-}C_{80}]^{2-}$ was studied. $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ displayed nucleophilic reactivity similar to that of $[Lu_3N@I_h\text{-}C_{80}]^{2-}$.

Theoretical studies of the $Sc_3N@I_h$-C_{80} monoanion showed that most of the spin density (up to 64%) is localized on the Sc_3N cluster in the preferred cluster orientation.[58] For $[Lu_3N@I_h\text{-}C_{80}]^{-}$, however, the amount of spin density on the carbon cage is much larger, in good agreement with electron paramagnetic resonance experiments (42% on Lu_3N and 58% on the cage for the lowest-energy isomer; other orientational isomers with relative energies within 2 kcal mol^{-1} show as much as 90% of the spin density on the cage).[72,73] The singly occupied MOs (SOMOs) for the radical monoanions $[M_3N@I_h\text{-}C_{80}]^{-}$ (M = Sc, Lu), which are intimately related to the distribution of the spin densities, are depicted in Scheme 2. The low spin density on the C_{80} cage for $[Sc_3N@I_h\text{-}C_{80}]^{-}$ explains the low nucleophilicity.

Calculations were performed for both dianions and trianions of Sc_3N and Lu_3N EMFs possessing an I_h-C_{80} cage to analyze their potential nucleophilicities. Different orientations of the cluster for both EMF anions were studied, and the computed relative energies showed that for the dianions, one orientation is favored by more than 6 (M = Sc) and 5 (M = Lu) kcal mol^{-1} (see the Supporting Information). A similar result was observed for the trianions, but the relative energies with respect to the lowest-energy orientational isomer were reduced, especially in the case of M = Lu.

The HOMOs of the direduced EMFs are almost identical to the SOMOs of the monoreduced anions (Scheme 2), so for the lowest-energy orientations, the contribution of the fullerene cage is more important when M = Lu than when M = Sc. The same behavior was observed for the other three isomers, so the HOMO is more localized on the fullerene cage when M = Lu, providing a rationale for the drastically different nucleophilicities observed experimentally. No evidence of reactivity was observed for $[Sc_3N@I_h\text{-}C_{80}]^{2-}$, while $[Lu_3N@I_h\text{-}C_{80}]^{2-}$ led to substantial product yield.[74]

Scheme 2. Electronic Structures of Anionic $Sc_3N@I_h$-C_{80} and Anionic $Lu_3N@I_h$-C_{80} Species with the Most-Stable DFT-Optimized Structures



The spin densities of $[M_3N@I_h\text{-}C_{80}]^{3-}$ (M = Sc, Lu) were computed as shown in Scheme 2 and Table S2 in the Supporting Information. For the lowest-energy cluster orientational isomers of $[M_3N@I_h\text{-}C_{80}]^{3-}$ (M = Sc, Lu), the spin density is mainly localized on the carbon cage. Whereas for $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ there is a non-negligible 41% of the electron spin density localized on the Sc_3N cluster, there is almost no spin density (only 9%) on the Lu_3N cluster in $[Lu_3N@I_h\text{-}C_{80}]^{3-}$. For the other cluster orientations, which show somewhat higher energies than the most favored one, the spin density is mainly localized on the M_3N cluster. Since the spin density of the EMF would be a Boltzmann average of the different orientations of the cluster, the total spin density on the carbon cage is predicted to be larger for $[Lu_3N@I_h\text{-}C_{80}]^{3-}$ than for $[Sc_3N@I_h\text{-}C_{80}]^{3-}$. From the SOMOs of $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ and $[Lu_3N@I_h\text{-}C_{80}]^{3-}$, we also confirmed that the extra electron is more localized on the carbon cage for $[Lu_3N@I_h\text{-}C_{80}]^{3-}$ than for $[Sc_3N@I_h\text{-}C_{80}]^{3-}$. Therefore, $[Lu_3N@I_h\text{-}C_{80}]^{3-}$ is predicted to be more reactive with electrophilic reagents than $[Sc_3N@I_h\text{-}C_{80}]^{3-}$, as was the case for the corresponding dianions, but the reactivity of the latter should be enough to lead to observable products. A direct comparison of the SOMO of $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ with the HOMO of $[Sc_3N@I_h\text{-}C_{80}]^{2-}$ (Scheme 2) clearly shows that the former is more localized on the carbon cage than the latter. As expected, $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ should be more reactive with electrophiles than $[Sc_3N@I_h\text{-}C_{80}]^{2-}$, as observed experimentally.

Table 2. Relative Energies and HOMO and LUMO Energies for Different Orientational Isomers of [6,6]-$[Sc_3N@I_h$-$C_{80}(CHPh)]$ and Pristine $Sc_3N@I_h$-C_{80}[a]

	orientation (deg)[b]	E_{rel} (kcal mol^{-1})	E_{HOMO} (eV)	E_{LUMO} (eV)
I1	0	2.2	−5.61	−4.19
I2	0	13.2	−5.63	−4.21
I3	45	0.0	−5.59	−4.12
I4	90	0.3	−5.64	−4.28
I5	90	11.9	−5.46	−4.23
$Sc_3N@I_h$-C_{80}			−5.78	−4.58

[a] The labeling used here for the different orientations of the Sc_3N cluster (I1−I5) is the same as that used in refs 58 and 74. [b] Approximate angle between the Sc_3N plane and the plane constituted by the methyne carbon of the ligand and the two functionalized C atoms of the cage.

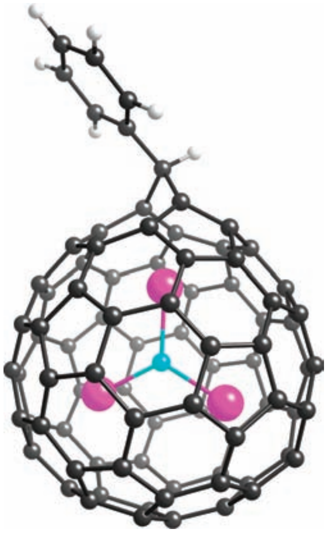


Figure 4. Representation of the structure of the lowest-energy orientational isomer of the [6,6]-$[Sc_3N@I_h$-$C_{80}(CHPh)]$ regioisomer.

The structure of product **1** was also optimized at the DFT level. Several orientations of the Sc_3N unit inside the functionalized fullerene were computed. One Sc atom is assumed to be pointing to the methano-C atom according to previous studies on related systems.[58] Other orientations show much higher energies. The relative energies of the optimized orientational isomers as well as their HOMO and LUMO energies are given in Table 2. The optimal structure corresponds to an open-cage fulleroid (Figure 4), for which the functionalized fullerene C···C distance is 2.162 Å. As for related systems, the [6,6] closed-cage regioisomer is not found to be a minimum when the Sc atoms are pointing to the functionalized C−C bond. Closed regioisomers are only found when the Sc atoms are further away from the reacting C−C bond, and they have higher energies than the open-cage fulleroid (isomer I5 in Table 2). Since there are several orientational isomers within an energy range of 2 kcal mol^{-1}, we can assume that the Sc_3N cluster can rotate fairly freely around an axis that crosses through the middle of the open C−C bond and the Sc−N bond. As shown in Table 2, the energies of the HOMO and LUMO change slightly with the position of the Sc_3N unit. The HOMOs of the three lowest-energy isomers are destabilized with respect to the HOMO of pristine $Sc_3N@I_h$-C_{80} by ca. 170 mV, which is in agreement with the CV experiment showing that the first oxidation potential of [6,6]-[$Sc_3N@I_h$-C_{80}(CHPh)] appears at a lower value than that of $Sc_3N@I_h$-C_{80}. The shift to more negative value of the first reduction potential can also be rationalized from the destabilization of the LUMO orbital of the pristine EMF after formation of the adduct.

CONCLUSION

An electroreductive synthetic method was successfully applied for the first time to prepare a functionalized $Sc_3N@I_h$-C_{80}. Electrochemically generated trianionic $Sc_3N@I_h$-C_{80} was reacted with benzal bromide to prepare the >CHPh-functionalized monoadduct, $Sc_3N@I_h$-C_{80}(CHPh) (**1**) in good yield. Compound **1** is a [6,6] open-cage adduct, as confirmed by a combination of MALDI−TOF MS, UV−vis−NIR, NMR, and CV characterizations and DFT calculations. The results prove that only trianionic $Sc_3N@I_h$-C_{80} is capable of undergoing nucleophilic reactions, while dianionic and monoanionic $Sc_3N@I_h$-C_{80} are unable to react. Computational analysis of the $Sc_3N@I_h$-C_{80} trianion and dianion show that the SOMO of $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ is more localized on the carbon cage than the HOMO of $[Sc_3N@I_h\text{-}C_{80}]^{2-}$, which is mainly localized on the Sc_3N cluster. The computational results are in excellent agreement with the observed experimental results.

While alternative and more traditional synthetic methods could be used to prepare **1** and **2**, the electrosynthetic method presented here offers the following advantages: (1) the reaction occurs at room temperature; (2) the method provides better control to prepare monoadducts and avoid multiadducts; and (3) the reaction times are short compared with more conventional synthetic methods. Therefore, electrosynthetic methods could be an important complement to the more conventional synthetic procedures for preparing endohedral fullerene derivatives.

EXPERIMENTAL SECTION

Materials and Methods. The procedures for obtaining pure $Sc_3N@C_{80}$ samples have been described previously.[75] Benzal bromide, *o*-DCB, and toluene were used as received. Tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu_4NPF_6) and tetra-*n*-butylammonium perchlorate (*n*-Bu_4NClO_4) were recrystallized from absolute ethanol and dried in vacuum before use. The purity of the compounds was verified using a Waters HPLC system equipped with a 2707 autosampler, a 2535 quaternary gradient module, a 2489 UV−vis detector, and a fraction collector III. MALDI−TOF MS was conducted on a Bruker Microflex LRF mass spectrometer. The NMR spectrum was recorded using a Bruker 300 MHz NMR spectrometer. The UV−vis−NIR spectra were recorded using a Cary 5000 UV−vis−NIR spectrophotometer. CV studies were conducted in a one-compartment cell connected to a BAS 100B workstation in a solution of *o*-DCB containing 0.05 M *n*-Bu_4NPF_6. A 2 mm diameter glassy carbon disk was used as the working electrode. Ferrocene (Fc) was added to the solution at the end of each experiment as an internal potential standard.

Synthesis and Isolation of 1 and 2. A 5 mg (4.5 mmol) sample of $Sc_3N@C_{80}$ was electrochemically reduced at −2.10 V versus a silver wire reference electrode in 15 mL of *o*-DCB containing 0.1 M *n*-Bu_4NClO_4 as the supporting electrolyte under an argon atmosphere. The potentiostat was turned off after the electrogeneration of $[Sc_3N@C_{80}]^{3-}$ was completed, and a 500-fold excess of benzal bromide (0.37 mL) was then added to the solution in one portion. The reaction was allowed to proceed for 2 h with stirring, and finally electrochemically oxidized at a potential of 0 V. The solvent was evaporated, and ca. 100 mL of methanol was added to precipitate the product and to remove the unreacted benzal bromide and the supporting electrolyte. The slurry was separated by filtration, and the residue was put in ca. 40 mL of toluene and sonicated. The soluble fraction was purified by HPLC using Buckyprep and 5PBB columns. A yield of 0.8 mg of **1** (27% based on consumed $Sc_3N@I_h$-C_{80}) was obtained. The yield of **2** was not determined because the exact amount of $Sc_3N@D_{5h}$-C_{80} in the original sample was not known. Data for **1**: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6, 25 °C, TMS): δ 7.74 (d, J = 7.5 Hz, 2H), 7.27 (m, 3H), 5.44 (s, 1H, C−H). MALDI−TOF MS (positive-ionization mode, 9-nitroanthracene as the matrix): $[M]^+$ m/z 1198.983.

Computational Details. The calculations were carried out using the DFT method with the ADF 2010 program.[76] The exchange and correlation functionals of Becke[77] and Perdew,[78] respectively, were used. Relativistic corrections were included by means of the ZORA formalism. Triple-ζ + polarization basis sets were employed to describe the valence electrons of C, N, H, and Sc.

ASSOCIATED CONTENT

Supporting Information

UV−vis−NIR spectra of $Sc_3N@I_h$-C_{80}, $[Sc_3N@I_h\text{-}C_{80}]^{-}$, $[Sc_3N@I_h\text{-}C_{80}]^{2-}$, and $[Sc_3N@I_h\text{-}C_{80}]^{3-}$ and the *xyz* coordinates for the lowest-energy structure of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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